(54) Title: MELT-STABLE LACTIDE POLYMER COMPOSITION AND PROCESS FOR MANUFACTURE THEREOF
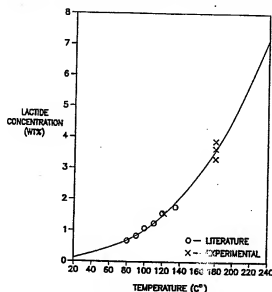
(57) Abstract

A lactide polymer composition combining compositional and purity limitations and catalyst optimization or addition of stabilizing agents resulting in a melt-stable polymer is disclosed. The melt-stable lactide polymer comprises a mixture of polylactide material having a number average molecular weight of at least about 10,000, residual lactide in concentration of less than about 2% and water in a concentration no greater than 1000 parts-per-million. A stabilizing agent in an amount sufficient to reduce depolymerization of the lactide polymer during melt-processing or alternatively, control of catalyst level at a molar ratio of monomer to catalyst greater than 3000:1 is also included in the melt-stable composition. A process for manufacture of a melt-stable lactide polymer composition includes polymerizing a lactide mixture and adding stabilizing agents sufficient to reduce depolymerization of the polylactide during melt-processing, followed by devolatilizing the polylactide to remove monomer and water.

MELT-STABLE LACTIDE POLYMER COMPOSITION
AND PROCESS FOR MANUFACTURE THEREOF
BACKGROUND OF THE INVENTION

1. Field of the Invention

5   The present invention relates to a melt-stable
lactide polymer composition and a process for
manufacturing such composition from lactide in the field
of degradable polymers.

2. Description of the Prior Art

10   The continued depletion of landfill space and
the problems associated with incineration of waste have
led to the need for development of truly biodegradable
polymers to be utilized as substitutes for non-
biodegradable or partially biodegradable petrochemical-
15 based polymers. The use of lactic acid and lactide to
manufacture a biodegradable polymer is well-known in the
medical industry. As disclosed by Nieuwenhuis et al.
(U.S. Pat. 5,053,485), such polymers have been used for
making biodegradable sutures, clamps, bone plates and
20 biologically active controlled release devices.
Processes developed for the manufacture of polymers to
be utilized in the medical industry have incorporated
techniques which respond to the need for high purity and
biocompatability in the final product. These processes
25 were designed to produce small volumes of high dollar-
value products, with less emphasis on manufacturing cost
and yield.

        In order to meet projected needs for
biodegradable packaging materials, others have
30 endeavored to optimize lactide polymer processing
systems. Gruber et al. (U.S. Pat. 5,142,023) disclose a
continuous process for the manufacture of lactide
polymers with controlled optical purity from lactic acid
having physical properties suitable for replacing
35 present petrochemical-based polymers for packaging,
paper-coating and other non-medical industry
applications.

Generally, manufacturers of polymers utilizing
processes such as those disclosed by Gruber et al. will
convert raw material monomers into polymer beads, resins
or other pelletized or powdered products. The polymer
5   in this form is then sold to end users who extrude,
blow-mold, cast films, blow films, thermoform,
injection-mold or fiber-spin the polymer at elevated
temperatures to form useful articles. The above
processes are collectively referred to as melt-
10 processing. Polymers produced by processes such as
those disclosed by Gruber et al., which are to be sold
commercially as beads, resins, powders or other non-
finished solid forms are generally referred to
collectively as polymer resins.

15   Prior to the present invention, it is believed
that there has been no disclosure of a combination of
composition control requirements which will lead to the
production of commercially viable lactide polymer resins
for the melt-processors.

20   It is generally known that lactide polymers or
polylactide are unstable. The concept of instability
though, has both negative and positive aspects. The
positive aspect is the biodegradation or other forms of
degradation to form non-hazardous products when lactide
25 polymers or articles manufactured from lactide polymers
are discarded or composted after completing their useful
life. The negative aspect of such instability is the
degradation of lactide polymers during processing at
elevated temperatures as, for example, during melt-
30 processing by end-user purchasers of polymer resins.
Thus, the same properties that make lactide polymers
desirable as replacements for non-degradable
petrochemical polymers also creates undesirable effects
during processing which must be overcome.

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Lactide polymer degradation at elevated
temperature has been the subject of several studies,
including: I. C. McNeill and H. A. Leiper, <u>Polymer
Degradation and Stability</u>, vol. 11, pp. 267-285 (1985);
5   I. C. McNeill and H. A. Leiper, <u>Polymer
Stability</u>, vol. 11, pp. 309-326 (1985); M. C. Gupta and
V. G. Deshmukh, <u>Colloid & Polymer Science</u>, vol. 260, pp.
308-311 (1982); M. C. Gupta and V. G. Deshmukh, <u>Colloid
& Polymer Science</u>, vol. 260, pp. 514-517 (1982); Ingo
10   Luderwald, <u>Dev. Polymer Degradation</u>, vol. 2, pp. 77-98
(1979); Domenico Garozzo, Mario Giuffrida, and Giorgio
Montaudo, <u>Macromolecules</u>, vol. 19, pp. 1643-1649 (1986);
and, K. Jamshidi, S. H. Hyon and Y. Ikada, <u>Polymer</u>, vol.
29, pp. 2229-2234 (1988).
15   It is known that lactide polymers exhibit an
equilibrium relationship with lactide as represented by
the reaction below:
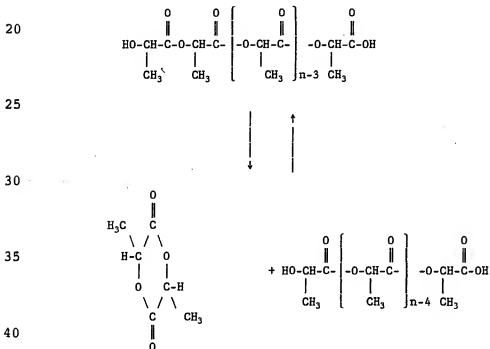
No consensus has been reached as to what the primary degradation pathways are at elevated processing temperatures. One of the proposed reaction pathways includes the reaction of a hydroxyl end group in a
5 "back-biting" reaction to form lactide. This equilibrium reaction is illustrated above. Other proposed reaction pathways include: reaction of the hydroxyl end group in a "back-biting" reaction to form cyclic oligomers, chain scission through hydrolysis of
10 the ester bonds, an intramolecular beta-elimination reaction producing a new acid end group and an unsaturated carbon-carbon bond, and radical chain decomposition reactions. Regardless of the mechanism or mechanisms involved, the fact that substantial
15 degradation occurs at elevated temperatures, such as those used by melt-processors, creates an obstacle to use of lactide polymers as a replacement for petrochemical-based polymers. It is apparent that degradation of the polymer during melt-processing must
20 be reduced to a commercially acceptable rate while the polymer maintains the qualities of biodegradation or compostability which make it so desirable. It is believed this problem has not been addressed prior to the developments disclosed herein.
25 As indicated above, polylactides have been produced in the past, but primarily for use in medical devices. These polymers exhibit biodegradability, but also a more stringent requirement of being bioresorbable or biocompatible. As disclosed by M. Vert, _Die_
30 _Inqwandte Makromolekulare Chemie_, vol. 166-167, pp. 155-168 (1989), "The use of additives is precluded because they can leach out easily in body fluids and then be recognized as toxic, or, at least, they can be the source of fast aging with loss of the properties which
35 motivated their use. Therefore, it is much more suitable to achieve property adjustment through chemical or physical structure factors, even if aging is still a

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problem." Thus, work aimed at the bioresorbable or
biocompatible market focused on polylactide and blends
which did not include any additives.

          Other disclosures in the medical area include
5 Nieuwenhuis (European Patent No. 0 314 245), Nieuwenhuis
   (U.S. Patent No. 5,053,485), Eitenmuller (U.S. Patent
   No. 5,108,399), Shinoda (U.S. Patent No. 5,041,529),
   Fouty (Canadian Patent No. 808,731), Fouty (Canadian
   Patent No. 923,245), Schneider (Canadian Patent No.
10 863,673), and Nakamura et al., Bio. Materials and
   Clinical Applications, Vol. 7, p. 759 (1987). As
   disclosed in these references, in the high value, low
   volume medical specialty market, polylactide or lactide
   polymers and copolymers can be given the required
15 physical properties by generating lactide of very high
   purity by means of such methods as solvent extraction
   and recrystallization followed by polymerization. The
   polymer generated from this high purity lactide is a
   very high molecular weight product which will retain its
20 physical properties even if substantial degradation
   occurs and the molecular weight drops significantly
   during processing. Also, the polymer may be
   precipitated from a solvent in order to remove residual
   monomer and catalysts. Each of these treatments add
25 stability to the polymer, but clearly at a high cost
   which would not be feasible for lactide polymer
   compositions which are to be used to replace inexpensive
   petrochemical-based polymers in packaging, paper-coating
   and other non-medical applications.
30   Furthermore, it is well-known that an increase
   in molecular weight generally results in an increase in
   a polymer's viscosity. A viscosity which is too high,
   can prevent melt-processing of the polymer due to
   physical/mechanical limitations of the melt-processing
35 equipment. Melt-processing of higher molecular weight
   polymers generally requires the use of increased
   temperatures to sufficiently reduce viscosity so that

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processing can proceed. However, there is an upper
limit to temperatures used during processing.
Increased temperatures increase degradation of the
lactide polymer, as the previously-cited studies
5   disclose.

Jamshidi et al., _Polymer_, Vol. 29, pp. 2229-
2234 (1988) disclose that the glass transition
temperature of a lactide polymer, T_g, plateaus at about
57°C for polylactide having a number average molecular
10   weight of greater than 10,000. It is also disclosed
that the melting point, T_m, levels off at about 184°C for
lactide polymers having a number average molecular
weight of about 70,000 or higher. This indicates that
at a relatively low molecular weight, at least some
15   physical properties of lactide polymers plateau and
remain constant.

Sinclair et al. (PCT Application No. WO
92/04413) disclose the use of residual monomer, lactic
acid or lactic acid oligomers to plasticize polylactide
20   polymers, with plasticizer levels of 2-60%. Loomis
(U.S. Patent No. 5,076,983) discloses a process for
manufacturing a self-supporting film in which the
oligomers of hydroxy acids are used as plasticizing
agents. Loomis and Sinclair et al. disclose that the
25   use of a plasticizer such as lactide or lactic acid is
beneficial to produce more flexible materials which are
considered to be preferable. Sinclair et al., however,
disclose that residual monomer can deposit out on
rollers during processing. Loomis also recognizes that
30   excessive levels of plasticizer can cause unevenness in
films and may separate and stick to and foul drums used
for casting such films. Thus, plasticizing as
recommended, negatively impacts melt-processability.

Accordingly, a need exists for a lactide
polymer composition which is melt-stable under the
elevated temperatures common to melt-processing. The
needed melt-stable polymer composition must also exhibit
5   sufficient compostability or degradability after its
useful life in order to be manufactured into useful
polymeric articles which are suitable as cost-
competitive replacements for similar articles made of
petrochemical-based polymers. Further, the melt-stable
10 polymer must be processable in existing melt-processing
equipment, by exhibiting sufficiently low viscosities at
melt-processing temperatures while polymer degradation
remains below a point of substantial degradation and
does not cause excessive fouling of processing
15 equipment. Furthermore, the polymer lactide must retain
its molecular weight, viscosity and other physical
properties within commercially-acceptable levels through
melt-processing. It will be further appreciated that a
need also exists for a process for manufacturing such
20 polymer compositions. The present invention addresses
these needs as well as other problems associated with
existing lactide polymer compositions and manufacturing
processes therefor. The present invention also offers
further advantages over the prior art, and solves other
25 problems associated therewith.

                    SUMMARY OF THE INVENTION
According to the present invention, a melt-
stable lactide polymer composition is provided,
30 preferably a generally amorphous melt-stable lactide
polymer composition comprising: a mixture of
polylactide material having a number average molecular
weight of at least 10,000 and preferably having a number
average molecular weight of from about 10,000 to about
35 300,000; lactide in a concentration of less than about
2% by weight; optionally, water in a concentration of
less than about 1,000 parts-per-million; and a

stabilizing agent in an amount sufficient to reduce
depolymerization of the polylactide polymer chains
during melt-processing to less than 2%. A process for
the manufacture of a melt-stable lactide polymer
5   composition is also provided.

            As previously disclosed, it is recognized in
the art that polymers of lactide degrade under
conditions of elevated temperature. It is also
recognized that commercially, a manufacturer of lactide
10 polymers utilizing a lactide monomer mixture as a raw
material will usually produce a lactide polymer resin to
be sold to end users or processors. The end user or
processor will purchase the resin and, in most
instances, melt-process the resin to produce useful
15 articles such as thin films, packaging materials, coated
papers, non-woven articles and any other useful article
that may be molded or extruded from the resin. It is
recognized however, that the polymer manufacturer may
also melt-process and sell the finished articles.

20   It is recognized that the exact method of melt-
processing is not relevant to the invention disclosed
herein. Rather it is only necessary to recognize that
the purchaser/processor of polymer resin must
necessarily process the resin at elevated temperature,
25 i.e., melt-process. Melt-processing of the resin
compositions of the present invention would, in most
instances, be processable in existing melt-processing
equipment which is used to process petrochemical-based
resins. The purchased lactide polymer resin must be
30 sufficiently stable through melt-processing (reduced
degradation) to give predictable and relatively constant
physical properties within the resulting product.
Further, the resin must not degrade and produce
excessive by-products which foul process equipment.

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Applicants have found that processability in
existing melt-process equipment generally requires that
the molecular weight of the resin be low enough so that
the viscosity is low enough at melt-processing
5 temperatures which do not cause substantial degradation.
The lower viscosity allows existing equipment to
mechanically process the resin. Reduced degradation
prevents fouling while maintaining physical properties.
This includes maintaining the initial molecular weight
10 and viscosity through melt-processing to avoid changes
in physical properties. Thus, the requirement of
processability is that the resin is sufficiently stable
that decomposition or degradation by-products do not
cause substantial fouling or plating out on existing
15 equipment. As to physical properties of the polymer
subsequent to melt-processing, the end user or melt-
processor must be able to rely on the consistency of the
resin to give relatively constant tensile strength,
percent elongation at break, impact strength, modulus of
20 elasticity, flexural modulus, yield and flexural
strength.

As disclosed herein, Applicants have developed
compositional requirements and methods of manufacture
which address the needs of the end user or melt-
25 processor. The resulting resin or lactide polymer
composition of the present invention is referred to
generally as a melt-stable lactide polymer. A melt-
stable lactide polymer is a polymer which has viscosity
low enough at melt-processing temperatures to be
30 processed in existing or commercially-available melt-
processing equipment and have sufficiently low rates of
degradation so that at the same temperatures the amount
of degradation during processing does not substantially
affect the physical properties of the final polymeric
35 article or cause significant plating or fouling on
processing equipment. These physical properties include
molecular weight and viscosity as well as others

disclosed herein. A test of melt stability would
include heating a devolatilized sample of lactide
polymer to 180°C at atmospheric pressure and measuring
the percent by weight generation of lactide in the first
5 hour. In a preferred composition of the present melt-
stable lactide polymers, the amount of lactide
generation is less than 3% by weight, preferably less
than 2% by weight and most preferably less than 1% by
weight in the first hour.

10   The melt-stable lactide polymer compositions of
the present invention comprise a plurality of
polylactide polymer chains having a number average
molecular weight from 10,000 to about 300,000. In a
more preferred composition, the number average molecular
15 weight ranges from about 15,000 to about 150,000. The
melt-stable lactide polymer composition preferably is
the reaction product of polymerizing a lactide mixture
comprising about 5% by weight to about 50% by weight
meso-lactide and about 95% by weight or less L-lactide.
20 With this preferred optical composition, the resulting
melt-stable lactide polymer is generally amorphous.

         The residual monomer concentration in the melt-
stable lactide polymer composition is less than 2% by
weight. The residual monomer is generally lactide
25 although lactic acid and other oligomers of lactic acid,
both cyclic and linear may be present as decomposition
by-products or residual contaminants from the
polymerization reaction. In a preferred composition,
the concentration of lactide in the polymer is less than
30 0.5% by weight. Contrary to previous disclosures,
Applicants have found that the monomer cannot be used as
a plasticizing agent in the resin of the present
invention due to significant fouling or plating out
problems in processing equipment. Thus, the residual
35 monomer concentration must be held below 2% by weight
and preferably below 1% by weight and most preferably
less than 0.2% by weight. It is believed that at these

low levels the residual monomer does not act as a
plasticizer.

The water concentration within the melt stable
lactide polymer composition is less than about 1,000
5   parts-per-million by weight. Applicants have found that
the presence of water in greater concentration causes
excessive loss of molecular weight and generation of
decomposition by-products which affect the physical
properties of the melt-processed polymer.

10   In a preferred composition, a stabilizing agent
in an amount sufficient to reduce depolymerization of
the polylactide polymer during melt-processing to less
than about 2% by weight generation of lactide in the
first hour at 180°C in atmospheric pressure is included
15   in the melt-stable lactide polymer composition (a
devolatilized sample is used to test melt-stability).
In preferred compositions the rate of generation is less
than 1.5% by weight and more preferably, less than 1.0%
by weight generation of lactide during the first hour at
20   180°C and atmospheric pressure.

The stabilizing agents may include antioxidants
and/or water scavengers. Preferable antioxidants are
phosphite-containing compounds, hindered phenolic
compounds or other phenolic compounds. Antioxidants
25   include such compounds as trialkyl phosphites, mixed
alkyl/aryl phosphites, alkylated aryl phosphites,
sterically hindered aryl phosphites, aliphatic
spirocyclic phosphites, sterically hindered phenyl
spirocyclics, sterically hindered bisphosphonites,
30   hydroxyphenyl propionates, hydroxy benzyls, alkylidene
bisphenols, alkyl phenols, aromatic amines, thioethers,
hindered amines, hydroquinones and mixtures thereof.

The water scavengers which may be utilized in
preferred embodiments of the melt-stable lactide polymer
composition include: carbodiimides, anhydrides, acyl
chlorides, isocyanates, alkoxy silanes, and desiccant
5   materials such as clay, alumina, silica gel, zeolites,
calcium chloride, calcium carbonate, sodium sulfate,
bicarbonates or any other compound which ties up water.
Preferably the water scavenger is degradable or
compostable.
10   In the manufacture of the melt-stable lactide
polymer compositions of the present invention, the
reaction to polymerize lactide is catalyzed. Many
catalysts have been cited in literature for use in the
ring-opening polymerization of lactones. These include
15 but are not limited to: SnCl$_2$, SnBr$_2$, SnCl$_4$, SnBr$_4$,
aluminum alkoxides, tin alkoxides, zinc alkoxides, SnO,
PbO, Sn (2-ethyl hexanoates), Sb (2-ethyl hexanoates),
Bi (2-ethyl hexanoates), Na (2-ethyl hexanoates)
(sometimes called octoates), Ca stearate, Mg stearate,
20 Zn stearate, and tetraphenyltin. Applicants have tested
several catalysts for polymerization of lactide at
180°C, which include: tin(II) bis(2-ethyl hexanoate)
[T-9, Atochem], dibutyltin diacetate [Fascat 4200®,
Atochem], butyltin tris(2-ethyl hexanoate) [Fascat 9102®,
25 Atochem], hydrated monobutyltin oxide [Fascat 9100®,
Atochem], antimony triacetate [S-21, Atochem], and
antimony tris(ethylene glycoxide) [S-24, Atochem]. Of
these catalysts, tin(II) bis(2-ethyl hexanoate),
butyltin tris (2-ethyl hexanoate) and dibutyltin
30 diacetate appear to be most effective.
Applicants have found the use of catalysts to
polymerize lactide significantly affects the stability
of the resin product. It appears the catalyst also is
effective at catalyzing the reverse depolymerization
35 reaction. To minimize this negative effect, in a
preferred composition, the residual catalyst level in
the resin is present in a molar ratio of monomer-to-

catalyst greater than 3000:1, preferably greater than
5,000:1 and most preferably greater than 10,000:1.
Applicants believe ratios as high as 20,000:1 could also
be utilized, however, polymerization time would be long.

5   Applicants have found that when catalyst level is
controlled within these parameters, catalytic activity
is sufficient to polymerize the lactide while
sufficiently low to enable melt-processing without
adverse effect when coupled with low residual monomer

10 level and low water concentration, as described above,
in polymers of molecular weight between about 10,000 to
about 300,000.

          Applicants have also found that catalyst
concentration may be reduced subsequent to

15 polymerization by precipitation from a solvent. This
produces a resin with reduced catalyst concentration.
In an alternative embodiment, the catalyst means for
catalyzing the polymerization of lactide to form the
polylactide polymer chains which was incorporated into

20 the melt-stable lactide polymer composition during
polymerization is deactivated by including in the melt-
stable lactide polymer composition a catalyst
deactivating agent in amounts sufficient to reduce
catalytic depolymerization of the polylactide polymer

25 chains. Such catalyst-deactivating agents include, but
are not limited to, hindered alkyl, aryl and phenolic
hydrazides, amides of aliphatic and aromatic mono- and
dicarboxylic acids, cyclic amides, hydrazones and
bishydrazones of aliphatic and aromatic aldehydes,

30 hydrazides of aliphatic and aromatic mono- and
dicarboxylic acids, bis-acylated hydrazine derivatives,
heterocyclic compounds and mixtures thereof.

          The preferred melt-stable lactide polymer
composition is the reaction product of polymerization of

35 lactide at a temperature greater than about 160°C.
Applicants have found that polymerization at higher
temperatures results in a characteristically different

polymer which is believed to have higher melt stability
and viscosity due to increased transesterification
during polymerization.

5 The process for manufacture of a melt-stable
lactide polymer comprises the steps of first providing a
lactide mixture wherein the mixture contains about 5% by
weight to about 50% by weight meso-lactide and about 95%
by weight or less L-lactide. This mixture is
10 polymerized to form polylactide and unreacted monomer in
the presence of a catalyst means for catalyzing the
polymerization of lactide to form polylactide. A
stabilizing agent, as disclosed above, may be added
simultaneously with or prior to the polymerizing of the
lactide to form polylactide. As previously disclosed,
15 the stabilizing agent is added in a sufficient amount to
reduce depolymerization of a devolatilized polylactide
sample during melt-processing to less than 2% by weight
generation of lactide in the first hour at 180°C and
atmospheric pressure Preferably, lactide generation is
20 less than 1.5% by weight, more preferably, less than
1.0% by weight. The lactide polymer is devolatilized to
remove unreacted monomer which may also be a by-product
of decomposition reactions and residual water which may
be present. Applicants recognize that the catalyst used
25 to polymerize lactide may be in the form of a soluble
catalyst or an insoluble solid, supported catalyst.

The process, preferably, also includes the step
of adding a molecular weight control agent to the
lactide prior to catalyzing the polymerization of the
30 lactide. Molecular weight control agents include active
hydrogen-bearing compounds such as lactic acid, esters
of lactic acid, alcohols, amines, glycols, diols, and
triols which function as chain-initiating agents. Such
molecular weight control agents are added in sufficient
35 quantity to control the number average molecular weight
of the polylactide to between about 10,000 and about
300,000, in preferred embodiments.

In a preferred process of the present
invention, the step of devolatilizing includes at least
reducing the concentration of unreacted lactide to less
than about 2% by weight and the concentration of water

5   to less than about 1,000 parts-per-million. Preferably,
the lactide concentration is reduced to less than 1% by
weight and more preferably less than 0.2% by weight.
        These and various other advantages and features
of novelty which characterize the present invention are

10 pointed out with particularity in the claims annexed
hereto and forming a part hereof. However, for a better
understanding of the invention, its advantages, and the
objects obtained by its use, reference should be made to
the drawings which form a further part hereof, and to

15 the accompanying descriptive matter, in which there are
illustrated and described preferred embodiments of the
present invention.

              BRIEF DESCRIPTION OF THE DRAWINGS
20   In the drawings, in which like reference
numerals indicate corresponding parts or elements of
preferred embodiments of the present invention
throughout the several views;
        Fig. 1 is a schematic representation of a

25 preferred process for the manufacture of a melt-stable
lactide polymer composition; and
        Fig. 2 is a graph showing the equilibrium
relationship between lactide and polylactide at various
temperatures.

30
    DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENT(S)
        As required, detailed embodiments of the
present invention are disclosed herein. However, it is
to be understood that the disclosed embodiments are

35 merely exemplary of the present invention which may be
embodied in various systems. Therefore, specific
details disclosed herein are not to be interpreted as

limiting, but rather as a basis for the claims and as a
representative basis for teaching one skilled in the art
to variously practice the present invention.

Lactide Polymers

5   Gruber et al. (U.S. Pat. 5,142,023) disclose a
continuous process for the manufacture of lactide
polymers with controlled optical purity from lactic
acid, which is incorporated herein by reference. As
disclosed by Gruber, the general route to producing a
10 lactide polymer begins with either lactic acid or an
ester of lactic acid which is first processed to form a
purified lactide (the cyclic dimer). The lactide may
vary in optical composition and levels of impurities.
This purified lactide stream is then polymerized to form
15 lactide polymer compositions utilized in the present
invention. The lactide polymer compositions and process
for manufacturing the lactide polymer compositions
disclosed herein focus on meeting the requirements of
the end user melt-processor of a lactide polymer resin
20 such as that produced from a process disclosed by Gruber
et al. As disclosed herein, the problems with
degradation and fouling during melt-processing of
lactide polymers are addressed through compositional
limits on impurities such as residual monomer, water and
25 catalyst along with the use of stabilizing agents and
catalyst-deactivating agents.

In general, according to the present invention,
a melt-stable lactide polymer and a process for
manufacturing a melt-stable lactide polymer are
30 disclosed. Lactide polymers are generally known and
cited for their usefulness due to biodegradable
properties. Furthermore, lactide polymers are
compostable as illustrated in Example 9 below. Several
mechanisms for each type of degradation have been
35 proposed, however, there is no consensus as to which
mechanisms are primary to the degradation of lactide
polymers. Applicants believe the hydrolysis of the

ester may be the key to or the first step in degradation
of a lactide polymer composition. The mechanism of
degradation is not key to the compositions of the
present invention, however it must be recognized that
5 such degradation makes lactide polymers desirable as
replacements for presently-utilized non-degradable
petrochemical-based polymers used for such useful
articles as packaging, paper-coating, thin film and
other injection-molded or blow-molded articles which are
10 discarded after their useful life.

        Applicants have found that the instability of
lactide polymers which leads to the beneficial
degradation discussed above also creates processing
problems. These processing problems include generation
15 of lactide monomer at elevated temperatures and loss in
molecular weight believed due to chain scission
degradation of the ester bonds and other
depolymerization reactions which are not completely
understood. Lactide polymer degradation at elevated
20 temperature has been the subject of several studies,
including: I. C. McNeill and H. A. Leiper, _Polymer
Degradation and Stability_, vol. 11, pp. 267-285 (1985);
I. C. McNeill and H. A. Leiper, _Polymer Degradation and
Stability_, vol. 11, pp. 309-326 (1985); M. C. Gupta and
25 V. G. Deshmukh, _Colloid & Polymer Science_, vol. 260, pp.
308-311 (1982); M. C. Gupta and V. G. Deshmukh, _Colloid
& Polymer Science_, vol. 260, pp. 514-517 (1982); Ingo
Luderwald, _Dev. Polymer Degradation_, vol. 2, pp. 77-98
(1979); Domenico Garozzo, Mario Giuffrida, and Giorgio
30 Montaudo, _Macromolecules_, vol. 19, pp. 1643-1649 (1986);
and, K. Jamshidi, S. H. Hyon and Y. Ikada, _Polymer_, vol.
29, pp. 2229-2234 (1988), which are incorporated herein
by reference. No consensus has been reached as to what
are the primary degradation pathways at elevated
35 processing temperatures. As previously disclosed, these
may include such pathways as equilibrium-driven
depolymerization of lactide polymers to form lactide and

chain scission through hydrolysis of the ester bonds
along with other pathways. For purposes of the present
invention, the exact mechanism of degradation at
elevated temperatures is not critical.

5   It is to be understood, however, that
degradation of lactide polymers is both beneficial and
detrimental. Benefits derive from degradability when
articles manufactured from such polymers are discarded.
The same or similar types of degradation are detrimental
10 if they occur during processing or prior to the end of
the article's useful life.

    Melt-Processing

          As disclosed by Gruber et al., a lactide
polymer may be extruded, blow-molded, injection-molded,
15 fiber-spun to a non-woven article or processed by any
other known melt-processing technique. In most
instances, it is recognized that a manufacturer of
lactide polymers from a lactide monomer will produce a
lactide polymer resin which is in the form of beads or
20 pellets which are sold to a melt-processor. The melt-
processor will convert the resin to a useful article
utilizing melt-processing encompassing any method of
converting a bead or pellet-type resin to a useful
article by elevating the temperature of the resin above
25 at least its glass transition temperature but normally
higher. Common melt-processing techniques include
extrusion, blow-molding, injection-molding, fiber-
spinning, film-blowing, film-casting and the like. It
is to be understood that the conditions of elevated
30 temperature used in melt-processing cause degradation of
lactide polymers during processing. Degradation under
melt-processing conditions is shown experimentally in
Example 1 based on equilibrium, Example 4 based on
catalyst concentration, Example 5 based on catalyst
35 activity, Example 7 based on use of stabilizers and
Example 8 based on moisture content. As can be seen in
these examples, it is understood that several factors

appear to affect the rate of degradation during melt-
processing. Applicants have addressed these factors in
a combination of compositional requirements and addition
of stabilizing or catalyst-deactivating agents to result
5 in a polymer of lactide which is melt-stable.

        Melt Stability

              The lactide polymers of the present invention
    are melt-stable. By "melt-stable" it is meant generally
    that the lactide polymer, when subjected to melt-
10 processing techniques, adequately maintains its physical
    properties and does not generate by-products in
    sufficient quantity to foul or coat processing
    equipment. The melt-stable lactide polymer exhibits
    reduced degradation relative to known lactide polymers.
15 It is to be understood that degradation will occur
    during melt-processing. The compositional requirements
    and use of stabilizing agents as disclosed herein
    reduces the degree of such degradation to a point where
    physical properties are not significantly affected by
20 melt-processing and fouling by impurities or degradation
    by-products does not occur. Furthermore, the melt-
    stable polymer must be melt-processable in melt-
    processing equipment such as that available
    commercially. Further, the polymer must retain
25 molecular weight and viscosity. The polymer must have
    sufficiently low viscosity at the temperature of melt-
    processing so that the melt-processing equipment may
    mechanically, for example, extrude the lactide polymer
    to a useful article. The temperature at which this
30 viscosity is sufficiently low must also be below a
    temperature at which substantial degradation occurs.

              As detailed in Example 12, a standard test for
    determining whether a lactide polymer is melt-stable
    includes placing a small portion of a devolatilized
35 sample of lactide polymer in a closed vial and placing
    such vial in a 180°C oil bath. A sample is taken at
    times of 15 minutes and 1 hour. The melt-stable lactide

polymer will show less than 2% lactide in the 15-minute
sample and, more preferably, less than 2% in the 1-hour
sample. It is more preferable that the stabilized
lactide polymer maintain lactide contents of less than
5   about 1 percent in both the 15-minute and 1-hour
samples. This comparison is relative to an equilibrium
concentration of about 3.6% by weight lactide at 180°C.

Polymer Composition

10   The melt-stable lactide polymer composition of
the present invention comprises polylactide polymer
chains having a number average molecular weight from
about 10,000 to about 300,000. In a preferred
composition, the number average molecular weight ranges
15 from about 15,000 to about 150,000. As detailed in
Example 3, it appears that the physical properties such
as modulus, tensile strength, percentage elongation at
break, impact strength, flexural modulus, and flexural
strength remain statistically constant when the lactide
20 polymer samples are above a threshold molecular weight.
The lower limit of molecular weight of the polymer
compositions of the present invention is set at a point
above the threshold in order to result in a lactide
polymer with predictable physical properties upon melt-
25 processing. As detailed in Example 16, there is a
practical upper limit on molecular weight based on
increased viscosity with increased molecular weight. In
order to melt-process a high molecular weight lactide
polymer, the melt-processing temperature must be
30 increased to reduce the viscosity of the polymer. As
pointed out in the Example, the exact upper limit on
molecular weight must be determined for each melt-
processing application in that required viscosities vary
and residence time within the melt-processing equipment
35 will also vary. Thus, the degree of degradation in each
type of processing system will also vary. Based on the
disclosure of Example 16, it is believed that one could

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determine the suitable molecular weight upper limit for
meeting the viscosity and degradation requirements in
any application.

The melt-stable lactide polymer compositions in
5   a preferred embodiment are the reaction product of
polymerizing a lactide mixture comprising about 5% by
weight to about 50% by weight meso-lactide and about 95%
by weight or less L-lactide. The optical composition
disclosed includes the benefit of utilizing meso-lactide
10   as disclosed by Gruber et al. Further, with this
preferred optical composition, the resulting melt-stable
lactide polymer is essentially amorphous. In preferred
compositions of the present invention, the melt-stable
lactide polymer is essentially non-crystalline or
15   essentially amorphous. As detailed in Example 9,
amorphous lactide polymers exhibit superior
degradability when subjected to a compost test as
detailed in the Example or when subjected to chemical
hydrolysis as detailed in the Example.

20   Applicants recognize that an essentially
amorphous lactide polymer may have some crystallinity.
Crystalline poly L-lactide exhibits an endotherm of
roughly 92 Joules per gram at its melting temperature of
170°-180°C. The melting point changes with composition.
25   The degree of crystallinity is roughly proportional to
the endotherm on melting. For.purposes of the present
invention, in preferred embodiments, it is meant by an
essentially amorphous or non-crystalline polylactide to
be a polylactide or lactide polymer which either
30   exhibits no melting endotherm in the temperature range
of 130°-200°C or which has an energy uptake of less than
10 Joules per gram if an endotherm is present.

The residual monomer concentration in the melt-
stable lactide polymer composition is less than about 2%
35   by weight. In a preferred composition the concentration
of lactide in the polymer is less than 1% by weight and
more preferably less than 0.5% by weight. Contrary to

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disclosures in the art, Applicants have found that the
monomer cannot be used as a plasticizing agent in the
resin of the present invention due to significant
fouling or plating out problems in processing equipment.
5 As detailed in Example 10, it is believed the low levels
of monomer concentration do not plasticize the final
polymer.

The water concentration within the melt-stable
lactide polymer composition is less than about 1,000
10 parts-per-million and more preferably less than 200
parts-per-million. As detailed in Example 8, the
polymer melt-stability is significantly affected by
moisture content. Thus, the melt-stable polymer of the
present invention must have the water removed prior to
15 melt-processing. Applicants recognize that water
concentration may be reduced prior to processing the
polymerized lactide to a resin. Thus, moisture control
could be accomplished by packaging such resins in a way
which prevents moisture from contacting the already-dry
20 resin. Alternatively, the moisture content may be
reduced at the melt-processor's facility just prior to
the melt-processing step in a dryer. Example 8 details
the benefit of drying just prior to melt-processing.
Example 11 details the problems encountered due to water
25 uptake in a polymer resin if not stored in a manner in
which moisture exposure is prevented or dried prior to
melt-processing. As detailed in these examples,
Applicants have found that the presence of water causes
excessive loss of molecular weight and generation of
30 decomposition by-products which may affect the physical
properties of the melt-processed polymer.

In a preferred composition of the present
invention, a stabilizing agent in an amount sufficient
to reduce depolymerization of the polylactide polymer
35 during melt-processing to less than 2% by weight
generation of lactide from devolatilized sample in the
first hour at 180°C and atmospheric pressure is included

in the melt-stable polymer composition. More
preferably, the amount of lactide generated is less than
1% by weight in thee first hour and most preferably less
than 0.5% by weight in the first hour. The stabilizing
5 agents recognized as useful in the present polymer
compositions may include antioxidants and/or water
scavengers. Preferable antioxidants are phosphite-
containing compounds, hindered phenolic compounds or
other phenolic compounds. Antioxidants include such
10 compounds as trialkyl phosphites, mixed alkyl/aryl
phosphites, alkylated aryl phosphites, sterically
hindered aryl phosphites, aliphatic spirocyclic
phosphites, sterically hindered phenyl spirocyclics,
sterically hindered bisphosphonites, hydroxyphenyl
15 propionates, hydroxy benzyls, alkylidene bisphenols,
alkyl phenols, aromatic amines, thioethers, hindered
amines, hydroquinones and mixtures thereof. As detailed
in Example 7, many commercially-available stabilizing
agents have been tested and fall within the scope of the
20 present melt-stable lactide polymer composition.
        The water scavengers which may be utilized in
preferred embodiments of the melt-stable lactide polymer
composition include: carbodiimides, anhydrides, acyl
chlorides, isocyanates, alkoxy silanes, and desiccant
25 materials such as clay, alumina, silica gel, zeolites,
calcium chloride, calcium carbonate, sodium sulfate,
bicarbonates or any other compound which ties up water.
Preferably the water scavenger is degradable or
compostable. Example 13 details the benefits of
30 utilizing a water scavenger.
        In the manufacture of the melt-stable lactide
polymer compositions of the present invention, the
reaction to polymerize lactide is catalyzed. Many
catalysts have been cited in literature for use in the
35 ring-opening polymerization of lactones. These include
but are not limited to: $SnCl_2$, $SnBr_2$, $SnCl_4$, $SnBr_4$,
aluminum alkoxides, tin alkoxides, zinc alkoxides, SnO,

PbO, Sn (2-ethyl hexanoates), Sb (2-ethyl hexanoates),
Bi (2-ethyl hexanoates), Na (2-ethyl hexanoates)
(sometimes called octoates), Ca stearates, Mg stearates,
Zn stearates, and tetraphenyltin. Applicants have also
5   tested several catalysts for polymerization of lactide
at 180°C which include: tin(II) bis(2-ethyl hexanoate)
[T-9, Atochem], dibutyltin diacetate.[Fascat 4200⁰,
Atochem], butyltin tris(2-ethyl hexanoate) [Fascat 9102⁰,
Atochem], hydrated monobutyltin oxide [Fascat 9100⁰,
10   Atochem], antimony triacetate [S-21, Atochem], and
antimony tris(ethylene glycoxide) [S-24, Atochem]. Of
these catalysts, tin(II) bis(2-ethyl hexanoate),
butyltin tris(2-ethyl hexanoate) and dibutyltin
diacetate appear to be most effective.
15   Applicants have found the use of catalysts to
polymerize lactide significantly affects the stability
of the resin product. It appears the catalyst as
incorporated into the polymer also is effective at
catalyzing the reverse depolymerization reaction.
20   Example 4 details the effect of residual catalyst on
degradation. To minimize this negative effect, in a
preferred composition, the residual catalyst level in
the resin is present in a molar ratio of monomer-to-
catalyst greater than 3,000:1, preferably greater than
25   5,000:1 and most preferably greater than 10,000:1.
Applicants believe a ratio of 20,000:1 may be used, but
polymerization will be slow. Optimization of catalyst
levels and the benefits associated therewith are
detailed in Example 14. Applicants have found that when
30   catalyst level is controlled within these parameters,
catalytic activity is sufficient to polymerize the
lactide while sufficiently low to enable melt-processing
without adverse effect when coupled with low residual
monomer level and low water concentration as described
35   above in polymers of molecular weight between 10,000 to
about 300,000. It is believed in most applications the
addition of a stabilizing agent may be unnecessary if

25

catalyst level is optimized.

        Applicants have also found that catalyst
concentration may be reduced subsequent to
polymerization by precipitation from a solvent. Example
5 15 demonstrates potential catalyst removal by
precipitation from a solvent. This produces a resin
with reduced catalyst concentration. In an alternative
embodiment, the catalyst means for catalyzing the
polymerization of lactide to form the polylactide
10 polymer chains which was incorporated into the melt-
stable lactide polymer composition during polymerization
is deactivated by including in the melt-stable lactide
polymer composition a catalyst deactivating agent in
amounts sufficient to reduce catalytic depolymerization
15 of the polylactide polymer chains. Example 5 details
the benefits of utilizing a catalyst deactivating agent.
Such catalyst-deactivating agents include hindered,
alkyl, aryl and phenolic hydrazides, amides of aliphatic
and aromatic mono- and dicarboxylic acids, cyclic
20 amides, hydrazones and bishydrazones of aliphatic and
aromatic aldehydes, hydrazides of aliphatic and aromatic
mono- and dicarboxylic acids, bis-acylated hydrazine
derivatives, and heterocyclic compounds. A preferred
metal deactivator is Irganox® MD1024 from Ciba-Geigy.
25   In an alternative embodiment, the catalyst
concentration is reduced to near zero by utilizing a
solid-supported catalyst to polymerize lactide. The
feasibility of utilizing such catalyst is detailed in
Example 2. It is believed catalysts which may be
30 utilized include supported metal catalysts, solid acid
catalysts, acid clays, alumina silicates, alumina,
silica and mixtures thereof.

        A preferred melt-stable lactide polymer
composition is the reaction product of polymerization of
35 lactide at a temperature greater than about 160°C.
Applicants have found that polymerization at higher
temperatures result in a characteristically different

polymer which is believed to have higher melt stability
due to increased transesterification during
polymerization. The benefits of higher temperature
polymerization are detailed in Example 6.

5   Melt-Stable Lactide Polymer Process
           The process for the manufacture of a melt-
stable lactide polymer comprises the steps of first
providing a lactide mixture wherein the mixture contains
about 5% by weight to about 50% by weight meso-lactide

10   and about 95% by weight or less L-lactide. Such
purified lactide stream may be such as that produced in
the process disclosed by Gruber et al., although the
source of lactide is not critical to the process of the
present invention.

15   The lactide mixture is polymerized to form a
lactide polymer or polylactide with some residual
unreacted monomer in the presence of a catalyst means
for catalyzing the polymerization of lactide to form
polylactide. Catalysts suitable for such polymerization

20   have been listed previously. The concentration of
catalysts utilized may be optimized as detailed in the
following examples and discussed previously.
           In a preferred embodiment, a stabilizing agent
as disclosed above, which may be an antioxidant and/or a

25   water scavenger is added to the lactide polymer. It is
recognized that such stabilizing agents may be added
simultaneously with or prior to the polymerization of
the lactide to form the lactide polymer. The
stabilizing agent may also be added subsequent to

30   polymerization.
           As previously disclosed, the stabilizing agent
is added in a sufficient amount to reduce
depolymerization of polylactide during melt-processing
is less than 2% by weight generation of lactide from a

35   devolatilized sample in the first hour at 180°C and
atmospheric pressure. More preferably, the stabilizing
agent controls lactide generation is less than 1% by

weight and most preferably less than about 0.5% by
weight in the first hour at 180°C and atmospheric
pressure. Alternatively, the control of catalyst
concentration to optimize the balance between necessary
5   catalytic activity to produce polylactide versus the
detrimental effects of catalytic depolymerization or
degradation of the lactide polymer may be utilized to
prevent the need for adding a stabilizing agent.
          The lactide polymer is then devolatilized to
10   remove unreacted monomer which may also be a by-product
of decomposition reactions or the equilibrium-driven
depolymerization of polylactide. Any residual water
which may be present in the polymer would also be
removed during devolatilization, although it is
15   recognized that a separate drying step may be utilized
to reduce the water concentration to less than about
1,000 parts-per-million. The devolatilization of the
lactide polymer may take place in any known
devolatilization process. The key to selection of a
20   process is operation at an elevated temperature and
usually under conditions of vacuum to allow separation
of the volatile components from the polymer. Such
processes include a stirred tank devolatilization or a
melt-extrusion process which includes a devolatilization
25   chamber and the like.
          In a preferred process for manufacture of a
melt-stable lactide polymer composition, the process
also includes the step of adding a molecular weight
control agent to the lactide prior to catalyzing the
30   polymerization of the lactide. Molecular weight control
agents include active hydrogen-bearing compounds, such
as lactic acid, esters of lactic acid, alcohols, amines,
glycols, diols and triols which function as chain-
initiating agents. Such molecular weight control agents
35   are added in sufficient quantity to control the number
average molecular weight of the polylactide to between
about 10,000 and about 200,000.

      Next referring to Figure 1 which illustrates a
preferred process for producing a melt-stable lactide
polymer composition. A mixture of lactides enters a
mixing vessel (3) through a pipeline (1). A catalyst
5 for polymerizing lactide is also added through a
pipeline (13). Within mixing vessel (3) a stabilizing
agent may be added through a pipeline (2). A water
scavenger may also be added through the pipeline (2).
The stabilized lactide mixture is fed through a pipeline
10 (4) to a polymerization process (5). The polymerized
lactide or lactide polymer leaves the polymerization
process through a pipeline (6). The stream is fed to a
second mixing vessel (8) within which a stabilizing
agent and/or catalyst deactivating agent may be added
15 through a pipeline (7). The stabilized lactide polymer
composition is then fed to a devolatilization process
(10) through a pipeline (9). Volatile components leave
the devolatilization process through a pipeline (11) and
the devolatilized lactide polymer composition leaves the
20 devolatilization process (10) in a pipeline (12). The
devolatilized lactide composition is fed to a resin-
finishing process (14). Within the resin-finishing
process the polymer is solidified and processed to form
a pelletized or granular resin or bead. Applicants
25 recognize the polymer may be solidified and processed to
form resin or bead first, followed by devolatilization.
The resin is then fed to a drying process (16) by
conveyance means (15). Within the drying process (16)
moisture is removed as a vapor through pipeline (17).
30 The dried lactide polymer resin leaves the drying
process (16) by a conveyance means (18) and is fed to a
melt-processing apparatus (19). Within the melt-
processing apparatus (19) the resin is converted to a
useful article as disclosed above. The useful article
35 leaves the melt-processing apparatus (19) through a
conveyance means (20).

Experimental

The following examples further detail
advantages of the system disclosed herein:

5   EXAMPLE 1:
    Lactide and Polylactide Equilibrium Concentrations

Experiments were conducted to determine the
equilibrium concentration of lactide and polylactide at
different temperatures. In these experiments a sample
10 of lactide was polymerized in the presence of a catalyst
(tin (II) bis(2-ethyl hexanoate) and held at a fixed
temperature for 18 hours or greater. Beyond this time
the residual monomer concentration is believed
essentially constant. The content of residual monomer
15 was determined by GPC analysis. GPC analysis was
conducted with an Ultrastyragel® column from Waters
Chromatography. The mobile phase was chloroform. A
refractive index detector with molecular weight
calibration using polystyrene standards was used. The
20 GPC temperature was 35°C. Data analysis was completed
using the software package Baseline, model 810, version
3.31.

The results of tests conducted on several
samples at various temperatures are summarized in the
25 graph of Fig. 2 as indicated by X's on such graph. Also
plotted on the graph of Fig. 2 are data points cited in
A. Duda and S. Penczek, _Macromolecules_, vol. 23, pp.
1636-1639 (1990) as indicated by circles on the graph.
As can be seen from the graph of Fig. 2, the equilibrium
30 concentration, and thus the driving force behind the
depolymerization of polylactide to form lactide,
increases dramatically with increased temperature.
Thus, melt-processing at elevated temperatures results
in degradation of the lactide polymer to form lactide on
35 the basis of equilibrium alone. For example, lactide
concentrations below about 2% cannot be directly
obtained at temperatures of 140°C or above due to the

identified equilibrium relationship between lactide and
polylactide.

EXAMPLE 2:

5   Lactide Polymerization in the Presence
                of a Solid Supported Catalyst

     Tin (II) Oxide

           24 grams of L-lactide and 6 grams of D,L-
10   lactide were combined in a round bottom flask with 0.033
     grams of Tin (II) oxide, as a fine powder. This
     corresponds to the catalyst level of 852:1, molar ratio
     lactide to tin. The flask was then purged with dry
     nitrogen 5 times. This was lowered into an oil bath at
15   160°C with magnetic stirring. Polymerization time was 8
     hours.

     Amberlyst 36

           24 grams of L-lactide and 6 grams of D,L-
     lactide were combined in a round bottom flask with 1.06
20   grams of Amberlyst 36 resin beads. The flask was purged
     5 times with dry nitrogen. The flask was lowered into
     an oil bath at 140°C with magnetic stirring.
     Polymerization time was 8 hours. The resin was a stated
     proton content of 1 Meq/gram dry weight resin. The
25   resin was prepared by rinsing 2 times with 10 volumes
     dry methanol, then dried for several hours under high
     vacuum for several hours at 40°C.

           The polymerization results are shown below:

30   TABLE 1

Sample	Mn	Mw	PDI	% Conversion
Tin (II) Oxide	77,228	103,161	1.34	54.0
35
Amberlyst	1,112	1,498	1.34	73.5

           Polylactide samples with various molecular
     weights and optical compositions were prepared by
40   polymerizing blends of L-lactide and meso-lactide at
     180°C under nitrogen in a 1-gallon sealed reactor.

Tin(II) bis(2-ethyl hexanoate) catalyst was added at a
monomer-to-catalyst ratio of 10,000:1. After about 1
hour the molten polymer was drained from the reactor
using nitrogen pressure. The sample was poured into a
5 pan and placed in a vacuum oven at about 160°C for about
4 hours to bring the reaction to near equilibrium
levels.

        The samples were ground and analyzed by GPC
(the method of Example 1) to determine the initial
10 molecular weight. Portions of the samples were then
dried under vacuum and processed in an injection molding
apparatus (New Britian 75 from New Britian Machine Co.)
to produce standard test bars for physical property
testing. The results of physical property testing are
15 shown in Table 2 on the following page. The physical
property tests were made according to ASTM methods D
638, D 256, and D 790. The reported results are the
averages of several tests.

        Samples of the test bars after injection
20 molding were again analyzed by GPC for molecular weight
as a measure of the effect of one type of melt-
processing on polymer degradation. Other portions of
the test bars were reground and tested in a capillary
viscometer to determine the melt-viscosity. These
25 results are also included in Table 2.

        Statistical analysis of the data revealed no
correlations which were statistically significant
between either optical composition or molecular weight
and the mechanical properties of modulus, tensile
30 strength, percentage elongation at break, notched Izod
impact strength, flexural modulus, or flexural strength.
The independence of these properties on molecular weight
indicates that all of these samples were above a
"threshold" molecular weight required to achieve the
35 intrinsic properties of the polymer in a preferred
composition.

        The viscosity data show significant

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correlations with molecular weight. This dependence
documents the practical limitation and necessity of
controlling polymer molecular weight below an upper
limit at which it is impractical to melt-process the
5 polymer. At high molecular weight, high viscosity
prevents processing by standard melt-processing
equipment. Increases in temperature to reduce viscosity
dramatically increase polymer degradation which is also
unacceptable.

TABLE 2

Sample I.D.	Meso Lactide In Blend, Wt%	Initial Molecular Weight	Molecular Weight After Injection Molding	Initial IV (dl/g)	Final IV (dl/g)	Viscosity at 173°C (Pa·S) Shear Rate 100 S⁻¹	Shear Rate 1000 S⁻¹
6	40	59000	41000	0.77	0.86	5.5	2.9
5	10	81000	54000	0.85	0.88	10.4	7.2
4	20	69000	59000	1.05	0.91	10.4	7.2
8	10	146000	64000	1.76	1.02	15.7	10.0
9	40	83000	68000	1.11	0.97	12.6	8.1
7	20	116000	71000	1.57	1.16	36.0	12.9
10	20	146000	83000	1.65	1.19	35.8	15.8

Mechanical Properties of Injection Molded Samples

Sample I.D.	Tensile Strength (Yld) PSI	Modulus MPSI	% Elongation at Break	IZOD Impact ft·lb/in	Flexural Modulus MPSI	Flexural Strength PSI
6	6600	0.55	3.3	0.39	0.53	11300
5	7800	0.56	3.5	0.46	0.54	12500
4	7600	0.56	3.9	0.32	0.53	12500
8	7700	0.55	3.4	0.47	0.53	12400
9	6700	0.59	3.1	0.42	0.52	10600
7	7400	0.56	3.3	0.45	0.51	12400
10	6700	0.55	3.0	0.47	0.52	9900

34

EXAMPLE 4:

Effect of Residual Catalyst on Polymer Degradation

Polymer samples were prepared at four levels of
catalyst, corresponding to monomer to catalyst molar
5   ratios of 5,000:1, 10,000:1, 20,000:1, and 40,000:1.
The catalyst utilized was tin (II) bis(2-ethyl
hexanoate). These samples were then subjected to
heating in a TGA apparatus (TA Instruments, Inc., model
951 thermogravometric analyzer with a DuPont 9900
10 computer support system) with a nitrogen purge.
Isothermal conditions of 200°C for 20 minutes were used.
The samples were then analyzed by GPC with a viscosity-
based detector and a universal calibration curve to
determine the extent of breakdown in molecular weight.
15 The GPC apparatus for this test was a Viscotek Model 200
GPC and a Phenomenex column. The TGA analysis typically
resulted in about a 5% loss in weight and molecular
weight drops of 0 to 70%.

The number average molecular weights were
20 converted to a milliequivalent per kilogram basis
$(1,000,000/Mn)$ in order to calculate a rate of chain
scission events. The results below represent averages
of 2-4 replicates on each of the four samples.

25   TABLE 3

Catalyst level (monomer/catalyst)	Scission Rate (meq/kg*min)
5,000	1.33
10,000	0.62
20,000	0.44
40,000	0.12

35 The rate of chain scission was directly proportional to
the residual catalyst level, demonstrating the
detrimental effect of catalyst activity on melt-
stability under conditions similar to melt-processing.
This instability, however, is distinguished from the
40 instability due to the equilibrium relationship between
lactide and polylactide detailed in Example 1, in that

loss of molecular weight due to catalytic
depolymerization by chain scission is evident.

EXAMPLE 5:
Catalyst Deactivation Experiment

5   Two runs were made in a laboratory Parr
reactor. Lactide feed was 80% L-lactide and 20% D,L-
lactide. Molecular weight was controlled by adding a
small quantity of lactic acid, the target molecular
weight was 80,000 Mn.

10   Lactide was charged to the reactor as a dry
mix, the reactor was purged 5 times with nitrogen, and
heated up to 180°C. At this point catalyst (5000:1
monomer to catalyst molar ratio, Fascat® 2003) was
charged through a port in the top of the reactor. The
15 reaction was allowed to proceed for 70 minutes at 180°C,
with mechanical agitation. Conversion at this point was
93-94%, close to the equilibrium value at 180°C of 96%
polylactide from Figure 2. This point is considered t-
zero, designating the completion of the polymerization
20 reaction and the beginning of the mixing time.

In the control experiment, a sample was taken
and the mixture was held at temperature with continued
agitation. Samples were taken periodically through a
port in the reactor bottom. After 4 hours the reactor
25 was drained.

In the example experiment, a sample was taken
and 0.25 weight % of a metal deactivator (Irganox® MD
1024®) was added through the catalyst addition port. The
mixture was held at temperature with continued agitation
30 and samples were withdrawn periodically. The reactor
was drained after 4 hours.

GPC analysis (utilizing the method of Example
1) for these samples was divided into three parts:
polymer with molecular weight over 4,000 (for which the
35 Mn and Mw numbers are reported), the percent oligomers
(comprising the region with molecular weight greater
than lactide but less than 4,000, as distinguished from

oligomers as defined by Loomis to include only oligomers
up to a molecular weight of 450), and percent lactide
(residual monomer). The structure of the oligomers was
not certain, but it is believed they were primarily

5 cyclic structures. It is also believed that the metal
deactivator, if unreacted, will elute with the oligomer
fraction. Quantification of the oligomer fraction is
difficult, because the GPC trace is near the baseline in
this region.

10   The analysis of the polymer samples as
withdrawn from the reactor at various time intervals for
the control and experimental compositions are shown
below in Table 4.

15   TABLE 4

Control	Mn	Mw	% Polymer	% Oligomer	% Monomer
20 t-zero	67,100	119,500	94	0	6.0
0.5 hr	62,500	119,000	95	0.7	3.9
1.0 hr	61,500	116,100	96	0	3.6
1.5 hr	56,000	111,600	95	1.5	3.3
2.0 hr	57,600	110,900	96	0.9	3.1
25 4.0 hr	51,400	105,400	94	3.3	3.1

Test	Mn	Mw	% Polymer	% Oligomer	% Monomer
30 t-zero	63,200	110,700	93	3.5	3.8
0.5 hr	52,100	108,600	92	4.6	2.9
1.0 hr	52,700	109,200	92	4.9	2.8
1.5 hr	53,400	107,200	93	4.0	3.1
2.0 hr	59,700	111,100	94	0.6	5.8
35 4.0 hr	51,200	107,300	91	6.1	3.3

The samples were then ground and placed in a
120°C oven under vacuum (pressure 0.1 inch Hg) for 14
hours. Sample analyses after this treatment are shown
below in Table 5.

5   TABLE 5

Control	Mn	Mw	% Polymer	% Oligomer	% Monomer
t-zero	45,500	88,500	98	2.2	0.0
0.5 hr	45,000	88,700	98	2.0	0.0
1.0 hr	43,900	87,200	98	2.0	0.0
1.5 hr	42,600	84,000	98	2.2	0.0
2.0 hr	42,000	85,200	97	3.2	0.0
4.0 hr	41,900	82,800	98	2.0	0.0

Test	Mn	Mw	% Polymer	% Oligomer	% Monomer
t-zero	39,300	76,700	96	4.0	0.0
0.5 hr	43,900	85,100	98	2.4	0.0
1.0 hr	55,300	98,600	96	3.8	0.0
1.5 hr	48,400	96,200	95	4.5	0.0
2.0 hr	48,900	101,900	95	5.0	0.0
4.0	50,600	101,900	94	5.6	0.0

In all cases the polymer was completely
devolatilized (0.0% residual lactide monomer). The data
also clearly show that the metal deactivator reduced the
degradation of polymer during the devolatilization step
(as indicated by the greater loss in Mn for the control
samples from Table 4 to Table 5 versus the Test
samples). One hour of mixing appears to be long enough
to develop most of the benefit.

The samples were stored at room temperature
under nitrogen for about 1 week and reanalyzed, as shown
below in Table 6.

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TABLE 6

Control	Mn	Mw	% Polymer	% Oligomer	% Monomer
t-zero	33,500	71,000	100	0.1	0.0
0.5 hr	43,400	95,800	99	1.0	0.0
1.0 hr	44,900	96,300	100	0.1	0.0
1.5 hr	45,900	95,000	100	0.0	0.0
2.0 hr	45,900	94,100	100	0.2	0.0
4.0 hr	43,100	90,100	99	1.3	0.0

Test	Mn	Mw	% Polymer	% Oligomer	% Monomer
t-zero	44,600	84,900	100	0.0	0.0
0.5 hr	45,300	90,600	99	1.2	0.0
1.0 hr	47,800	100,000	98	2.4	0.0
1.5 hr	46,600	98,900	96	3.5	0.0
4.0	57,700	110,200	96	4.0	0.3

Equilibrium lactide levels are estimated to be less than 0.2 weight % at room temperature. Consistent with that, essentially no lactide was observed in any of the samples (detection limit about 0.1 wt%). The oligomer content in the non-stabilized samples declined and some increase in molecular weight was noted, perhaps due to reincorporation of the (cyclic) oligomers into the polymer. The oligomer depletion reaction was inhibited in the stabilized polymers, with the extent of inhibition dependent on the length of time that the additive was mixed.

The samples were then reheated to 180°C in sealed vials and held for one hour as a simulation of melt-processing. Analysis of the samples after the heat treatment is given below in Table 7.

TABLE 7

Control	Mn	Mw	% Polymer	% Oligomer	% Monomer
t-zero	23,900	60,000	88	8.4	4.0
0.5 hr	23,900	59,600	90	7.7	2.7
1.0 hr	23,700	58,800	88	9.3	2.7
1.5 hr	24,700	58,000	86	10.0	3.8
2.0 hr	26,100	56,400	90	6.8	2.7
4.0 hr	24,800	58,700	92	6.6	1.9

Test	Mn	Mw	% Polymer	% Oligomer	% Monomer
t-zero	33,900	64,300	95	2.2	3.1
0.5 hr	17,900	34,600	94	4.8	1.7
1.0 hr	21,200	42,900	94	4.6	1.8
1.5 hr	29,200	56,900	98	0.5	1.8
2.0 hr	missing				
4.0 hr	35,700	71,400	95	3.7	1.7

The data for molecular weight show that if the metal deactivator is not mixed into the system long enough then it can have a detrimental impact on stability in the melt. The samples for which the mixing was at least 1.5 hours show no detrimental effect, and the 4 hour sample appears to be somewhat more stable than any of the others based on molecular weight alone. More importantly, the metal deactivator samples show significantly less lactide reformation than the control samples. This effect is gained even in the samples which were mixed for only 0.5 hour. The metals deactivated samples averaged only 1.8% lactide after one hour at 180°C, compared to an average of 3.0% lactide for the controls. The equilibrium level at 180°C is about 3.6% from Figure 2. Thus, the use of metal deactivators can reduce the troublesome reformation of lactide during melt-processing of the finished polymer.

EXAMPLE 6:

Effect of Increased Polymerization Temperature
on Polymer Characteristics

L-lactide (Boeringer Ingleheim, S-grade) was

5   used as received, meso-lactide (PURAC) was purified by
redistillation to remove traces of D- and L-lactide.
The melting point of the purified meso-lactide was 54°C.
Lactide mixtures were made up to the following ratios:
100% L-lactide, 90/10 L-lactide/meso-lactide, 70/30 L-

10 lactide/meso-lactide, 50/50 L-lactide/meso-lactide, and
100% meso-lactide. Catalyst level was 2,500:1 molar
ratio of monomer to tin added as Fascat® 9002. Lactic
acid was added as a molecular weight control agent to
target a number average molecular weight of 50,000 (the

15 same amount was added to all samples). Polymerization
times were estimated to obtain conversions of 50% and
90%. For 120°C this was 4 hours and 16 hours,
respectively. For 180°C these times were 10 minutes and
50 minutes, respectively. Below in Table 8 are the GPC

20 results (method of Example 1) of tests on the polymer
samples produced by this procedure.

TABLE 8

1/meso	Temp	Mn	Mw	PDI	%Conv
100% 1	120°C	31,014	33,774	1.09	53.2
		45,864	52,574	1.15	87.1
100% 1	180°C	27,785	32,432	1.17	46.7
		56,839	98,125	1.73	93.3
90/10	120°C	34,541	38,586	1.12	62.3
		29,222	34,466	1.18	89.3
90/10	180°C	31,632	35,713	1.13	48.5
		57,925	110,841	1.91	94.8
70/30	120°C	41,211	45,222	1.10	60.1
		58,284	71,257	1.22	89.1
70/30	180°C	32,292	37,401	1.16	53.8
		51,245	107,698	2.10	96.5
50/50	120°C	15,888	17,969	1.13	57.8
		25,539	31,834	1.25	90.6
50/50	180°C	34,375	42,018	1.22	62.5
		44,590	98,028	2.20	95.5
100% meso	120°C	33,571	40,635	1.21	73.4
		45,237	68,142	1.51	94.3
100% meso	180°C	30,976	42,987	1.39	67.6
		40,038	83,815	2.09	96.6

The results show that the ultimate number
average molecular weight was not significantly affected
by the temperature of polymerization, with an average of
41,000 at 120°C and 50,000 at 180°C. This implies that
each lactic acid molecule initiates about one polymer
chain, regardless of temperature. The ultimate weight
average molecular weight is, however, significantly
affected by temperature. At 120°C the weight average
molecular weight averaged 52,000 and at 180°C the
average was 100,000. This is believed to be due to a
relative increase in the rate of transesterification at
180°C. The polydispersity index (PDI) at high
conversion also reflects this, averaging 1.3 at 120°C
and 2.0 at 180°C. It is believed these differences

would have a significant effect on the melt-processing
characteristics of the polymer, with the higher weight
average molecular weight of the polymer produced at
180°C expected to translate into better melt strength
5   and processability.

        These experiments show that polymerization at a
higher temperature results in a polymer that is
characteristically different, even though the polymers
have a similar number average molecular weight, the
10 weight average molecular weight is much higher. This
difference is also reflected in the polydispersity index
(PDI). High temperature polymerization which gives a
higher weight average molecular weight will give a
higher melt strength and better processability. This is
15 believed due to increased transesterification rates
relative to polymerization rate. Further, the glass
transition temperature for the samples polymerized at
higher temperature is higher, further evidencing that
polymers of the same composition but polymerized at
20 higher temperatures are more melt-stable.

                        EXAMPLE 7:
             Experiments with Stabilizing Agents
                    and Metal Deactivators

25   Test 1
            Conditions: vial polymerization, (Lactide is
melted under a nitrogen-purged atmosphere in a round
bottom flask with stirring. Catalyst and additives are
added and aliquots of the mixtures are pipetted into
30 silanized glass vials. Typically 5-10 grams of reaction
mixture are used in a 16 ml. vial. The vials are
tightly capped and placed into a preheated oil bath.)
10,000:1 molar ratio of lactide-to-tin, tin(II) bis(2-
ethyl hexanoate) catalyst, 0.2 wt% Ultranox®626 in
35 tetrahydrofuran (THF). 180°C. Time was 90 minutes.
Purchased lactide was used.
            The control with tin only polymerized to 84%
conversion and reached a MWn of 31,700. The example

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with tin and Ultranox® polymerized to 83% conversion and
reached a MWn of 39,800; an increase of 26% over the
control.

     The control sample turned light yellow, the
5 sample with stabilizer remained colorless.

    Test 2

     Conditions: vial polymerization, 5000:1 molar
ratio of lactide to tin, tin(II) bis(2-ethyl hexanoate)
catalyst, 0.25 wt% Ultranox®626 (in THF). 180°C. Time
10 was 60 minutes. Pilot plant lactide was used.

     The control with tin alone polymerized to 67%
conversion and reached a MWn of 62,900. The example
with tin and Ultranox® polymerized to 66% conversion and
reached a MWn of 75800; an increase of 21% over the
15 control.

     A second example with tin(II) bis(2-ethyl
hexanoate), Ultranox®, and 0.50% of Irganox® 1076, which
is a phenolic antioxidant, polymerized to 66% conversion
and reached a number average molecular weight (MWn) of
20 74500; an increase of 18% over the control.

    · All samples were a dark yellow color, although
the samples with stabilizer had a slightly lower
absorbance at 300 nm.

    Test 3

25   Conditions: vial polymerization, 10,000:1
molar ratio of lactide to tin, tin(II) bis(2-ethyl
hexanoate) catalyst, 180°C, 80% L-lactide and 20% D,L-
lactide purchased from Henley and Aldrich, respectively.
Lactic acid was added to control molecular weight to
30 about 75,000 at full conversion. One sample included
0.25% Ultranox® 626 phosphite stabilizer, one included
0.25% Irganox® 1076 antioxidant, and one control sample.

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Samples were taken at various times and
analyzed by GPC for conversion and molecular weight (the
method of Example 1). The results are summarized in
Table 9 below.

TABLE 9

Time	Control		Irganox®		Ultranox®	
(hrs)	Mn	%conv	Mn	%conv	Mn	% conv
1	31,000	46	35,900	41	66,500	61
2	45,400	74	56,800	74	102,700	83
4	69,600	93	74,100	93	97,200	91
11	52,900	95	60,700	95	71,500	94

The sample with phosphite stabilizer
polymerized faster, shown by the higher conversion at 1
and 2 hours, and went to a higher molecular weight than
the control or the sample with Irganox. The phosphite
stabilized sample had a molecular weight more than 30%
higher than the control for all time periods.

Test 4

The experiment above was repeated to compare
the control to the phosphite-stabilized polymer, as
summarized in Table 10 below.

TABLE 10

Time	Control		Ultranox®	
(hrs)	Mn	%conv	Mn	%conv
1	36,600	37	71,500	59
2	51,700	70	95,200	85
4	64,400	91	103,700	94
8	58,100	96	95,700	94

The sample with phosphite stabilizer again
polymerized faster and went to a higher molecular weight
than the non-stabilized sample. The phosphite
stabilized sample had a molecular weight more than 60%
higher than the control for all time periods.

45

Test 5

        Conditions: vial polymerization, 5,000:1 molar
ratio of lactide to tin, tin(II) bis(2-ethyl hexanoate)
catalyst, 180°C, 80% L-lactide and 20% D,L-lactide
5   purchased from Henley and Aldrich. Lactic acid was
added to control number average molecular weight to an
estimated 80,000 at full conversion. One sample was run
with 0.25% Ultranox® 626 phosphite stabilizer, one with
0.25% Irganox® 1076 antioxidant, and one control sample.
10   Samples taken at various times and analyzed by
GPC (the method of Example 1) for conversion and
molecular weight. The results are tabulated in Table 11
below.

15   TABLE 11

Time	Control		Irganox®		Ultranox®	
(hrs)	Mn	%conv	Mn	%conv	Mn	% conv
1	83,600	76	121,900	83	162,300	87
4	74,400	93	104,300	95	123,900	96
24	40,200	96	52,000	96	96,900	97
48	34,200	97	30,400	96	56,500	96
72	25,000	96	22,400	96	69,500	96

        The phosphite-stabilized sample had a molecular
weight more than 60% higher than the control for all
time periods. After 72 hours it had a molecular weight
2.8 times higher than the control. The sample with
30 antioxidant showed an initial increase in molecular
weight, relative to the control, but the effect
disappeared after 48 hours.
        The phosphite stabilized sample was
significantly lighter in color than the control or the
35 antioxidant treated sample.

Test 6

        Conditions: vial polymerization, 5000:1 molar
ratio of lactide to tin, tin(II) bis(2-ethyl hexanoate)

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catalyst, 0.25 wt% Ultranox®626 (in THF). 180°C. Time
was two hours. Pilot plant lactide washed with
isopropyl alcohol was used.

     The control with tin alone polymerized to 95%
5 conversion and reached a number average molecular weight
of 118,000. The example with tin and Ultranox®
polymerized to 93% conversion and reached a number
average molecular weight of 151,000, an increase of 28%
over the control.

10

    <u>Test 7</u>
      Conditions: vial polymerization at 180°C.
5000:1 molar ratio of lactide to tin, tin(II) bis(2-
ethyl hexanoate) catalyst. Lactide was 80% L-lactide
15 and 20% D,L-lactide, purchased from Henley and from
Aldrich. Lactic acid was added to target the molecular
weight to an Mn of 80,000. All stabilizers were added
at 0.25 weight %. Molecular weight (number average) was
determined for samples pulled at 3 hours, while rate
20 constants were based on samples pulled at 1 hour. The
results of these screening tests on many stabilizing
agents following the above procedure are detailed below
in Table 12. Product designations in Table 12 are
tradenames or registered trademarks.

25

TABLE 12

Sample		Mn	% Conversion	Relative Rate
Control 1		65,000	95.9	90
Control 2		85,000	95.9	100
Control 3		76,000	96.6	100
Control 4		69,000	96.2	100
Control 5		74,000	96.8	110
Control 6		70,000	97.2	110
PHOSPHITES				
Ultranox 626	(GE)	103,000	96.8	100
Weston TDP	(GE)	64,000	70.0	60
Weston PDDP	(GE)	67,000	76.7	60
Weston PNPG	(GE)	92,000	94.1	100
Irgafos 168	(Ciba-Geigy)	95,000	95.3	120
Weston 618	(GE)	99,000	95.1	100
Sandostab P-EPQ	(Sandoz)	108,000	94.7	110
Weston TNPP	(GE)	88,000	97.9	130
PHENOLIC ANTIOXIDANTS				
Irganox 1010	(Ciba-Geigy)	95,000	97.5	110
Cyanox 1790	(Cyanamid)	98,000	96.9	120
BHT		87,000	96.5	130
Irganox 1076	(Ciba-Geigy)	121,000	97.8	130
Topanol CA	(ICI)	84,000	96.6	160
AMINES				
Tinuvin 123	(Ciba-Geigy)	65,000	94.8	70
Tinuvin 622	(Ciba-Geigy)	82,000	95.7	80
Naugard 445	(Uniroyal)	93,000	98.2	120
THIOETHER				
Mark 2140	(Witco)	77,000	97.0	120
METAL DEACTIVATORS				
Irganox MD1024	(Ciba-Geigy)	34,000	65.7	10
Naugard XL-1	(Uniroyal)	91,000	95.8	110

Note, that with a few exceptions, the phosphites and the phenolic antioxidants provide increased molecular weight with no reduction in

polymerization rate. Of the amines, only Naugard® 445
provided stabilization without a rate decrease. The
metal deactivators are expected to deactivate the
catalyst, as was observed for Irganox® MD1024. The
5 Naugard® XL-1 did not accomplish deactivation.

                          EXAMPLE 8:

   Polymer Melt Stability as a Function of Moisture Content
           Lactide, produced and purified in a continuous
10 pilot plant, was fed at a rate of 3 kg/hr to a
   continuous polymerization pilot plant. Catalyst was
   added with a metering pump at the rate of 1 part
   catalyst to 5000 parts lactide on a molar basis. The
   reaction system was blanketed with nitrogen. The
15 reactor vessels consist of two continuous stirred tank
   reactors (CSTR) in series. The first had a 1-gallon
   capacity and the second had a 5-gallon capacity. The
   reactors were run 60-80% liquid filled and at 170-180°C.
   Polymer melt pumps moved the liquid from CSTR 1 to CSTR
20 2, and from CSTR 2 through a die into a cooling water
   trough. The polymer strand thus produced was pulled
   from the trough by a pelletizer and stored as pellets.
           The pelletized polylactide was put into a
   drying hopper and dried at 40°C under flowing dry air.
25 Samples were pulled after one hour and four hours.
   These samples were then run through a single screw
   Brabender® extruder, with a retention time of
   approximately 3 minutes. Samples were analyzed for
   moisture by an automatic Karl Fischer apparatus and for
30 molecular weight by GPC (the method of Example 1). The
   results of these tests are documented in Table 13 below.

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TABLE 13

Sample	Extruder Temperature (C)	Weight Average Molecular Weight
Initial		63,000
Dried 1 hour (1200 ppm H_2O)	137	44,000
	145	48,000
	162	35,000
	179	30,000
Dried 4 hours (150 ppm H_2O)	140	63,000
	140	69,000
	160	65,000
	178	68,000

These results show the detrimental effect of
water in the lactide polymer resin during melt
polymerization and the need to properly dry the
polylactide before melt-processing.

EXAMPLE 9:
Degradation of Crystalline and
Amorphous Polylactide

Two literature references disclose poly(D,L-
lactide) to degrade faster than poly(L-lactide),
attributing the result to crystallinity of poly(L-
lactide). These are: Kulkarni et al., J. Biomed.
Mater. Res., vol. 5, pp. 169-181, (1971); Makino et al.,
Chem. Pharm. Bull., vol. 33, pp. 1195-1201, (1985). An
experiment was conducted to measure the effect of
crystallinity on polymer degradation and is detailed
below.

An amorphous polylactide sample (clear, and
less than 1% crystallinity based on DSC) and a
crystalline polylactide sample (opaque, and
approximately 50% crystallinity based on DSC) were
subjected to biodegradation in a compost test (50°C,
with aeration). The DSC apparatus was a TA Instruments,
Inc., model 910 differential scanning calorimeter with

DuPont 9900 computer support system typically programmed
to heating at a rate of 10°C per minute to 200°C. The
samples had different optical composition, with the
crystalline sample being more than 90% poly(L-lactide)
5   and the amorphous sample being less than 80% poly(L-
lactide) with the balance being either poly(D,L-lactide)
or poly(meso-lactide). Samples of each polymer were
subjected to a compost test which included mixing a
stabilized compost and providing a source of humidified
10   air while maintaining a temperature of about 50°C. The
amorphous sample was completely degraded after 30 days
of composting. The crystalline sample was only 23%
degraded based on carbon dioxide after the same period
of time.

15   Additional samples of these two polymers were
subjected to chemical hydrolysis at 50°C (hydrolysis is
believed to be the rate-limiting step in the
biodegradation process). The chemical hydrolysis
procedure included placing 0.1 gram polylactide in 100
20   ml of 0.2M phosphate buffer (pH = 7.4). The samples
were held for 1 week, then filtered, washed with
deionized water, and dried at 25°C under vacuum. The
initial weight average molecular weight for each sample
was about 70,000. After 1 week the amorphous sample had
25   a weight average molecular weight of 10,000 and the
crystalline sample had a weight average molecular weight
of 45,000, determined by GPC (the method of Example 1).
Neither sample had significant weight loss at this time.
         Both of these tests demonstrate that
30   degradation of crystalline polylactide is slower than
degradation of amorphous polylactide.

                     EXAMPLE 10:
         Effect of Monomer Concentration on Film Modulus
35   Polylactide was precipitated in methanol from a
chloroform solution in order to remove the residual
lactide monomer. GPC analysis (the method of Example 1)

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showed the precipitated polymer to contain 0.0% lactide.

The polymer was dissolved in chloroform to make
a 10 wt% solution, and lactide was added back to make 5
separate solutions which, after removing the chloroform,
5   are calculated to produce films containing 0.0, 0.2,
0.4, 1.0 and 4.0 wt% lactide in polylactide. These
solutions were solvent cast onto glass, dried overnight
at room temperature in a fume hood, and removed to a
vacuum oven. The films were hung in the vacuum oven and
10   dried at 30°C for 72 hours. GPC analysis of the vacuum-
dried films showed measured lactide levels of 0.0, 0.0,
0.0, 0.7 and 3.7 wt%.

The films were then tested for film modulus
using ASTM procedure D882.

15   The results are shown below in Table 14.

TABLE 14

% Lactide	Tensile (psi avg.)	Std. Dev.	% Elongation	Std. Dev.	Elastic Modulus (psi. avg.)	Std. Dev.
0	5490	636	2.85	0.14	730,000	103,000
0	6070	123	2.85	0.22	818,000	35,000
0	5670	227	2.75	0.27	779,000	44,000
0.7	5690	343	4.04	1.12	749,000	58,000
3.7	5570	458	3.33	1.43	738,000	66,000

EXAMPLE 11:

Rate of Water Uptake Versus Optical Composition

30   Samples of polylactide, made from 80% L-lactide
and 20% of either D,L-lactide or meso-lactide, were
ground to pass a 20 mesh screen. The samples were dried
and devolatilized under vacuum then removed to a
constant humidity chamber maintained at 24°C and 50%
35   relative humidity. The rate of moisture pick-up was
determined gravimetrically, with the final results
verified by Karl-Fischer water analysis. The rate of
moisture pickup is shown below in Table 15.

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TABLE 15

		Parts Per Million	
	Time		Weight Gain	
	(Minutes)	L/D,L Polymer	L/Meso Polymer
	10	600	1000
	30	1100	1500
	60	1500	1800
	120	1600	2100
	870	2100	2600
	Karl-Fischer	3000	2600

EXAMPLE 12:

Standard Test of Melt Stability

A standard test for determining melt stability is as follows:

A small sample (200 grams or less) of polymer is ground or pelletized and devolatilized by holding under vacuum (about 10 mm Hg) at a temperature of 130°C or less for 18 hours. At this point the residual lactide content should be 1 wt% or less. Portions (1-5 grams) of the devolatilized sample are then placed in a 16 ml sample vial, tightly capped, and placed in a 180°C oil bath. Samples are removed at times of 15 minutes and 1 hour and analyzed for lactide content by GPC or other appropriate techniques. Lactide which may collect on the cooler portions of the vial is included in the product work-up and test.

Melt-stabilized polylactide will show less than 2% lactide in the 15 minute sample, and more preferably less than 2% lactide in the 1 hour sample. The most highly stabilized polylactides will maintain lactide contents of less than 1% in both the 15 minute and 1 hour samples, preferably less than 0.5%. An unstabilized polylactide may reach the equilibrium lactide content at 180°C of 3.6 wt%, or may go even higher as lactide is driven from the polymer melt and collects on the cooler top walls of the vial.

EXAMPLE 13:

Water Scavenger Experiments

Dried polylactide pellets were processed in a
twin screw extruder to devolatilize and to prepare a
5   portion with 0.5% by weight of a water scavenger
(Stabaxol® P). The strands leaving the extruder are
cooled in a water trough and chopped into pellets.
Samples of the control and the test sample were then
analyzed by the Karl Fischer technique for moisture
10 content, with no drying. The control sample contained
1700 ppm water, the test sample had 450 ppm water. The
control sample was then dried under nitrogen at 40°C,
reducing the water content to 306 ppm. A vacuum-dried
control sample had 700 ppm water.

15   The as-produced test sample and the dried
control samples were then processed in a 1/2" single
screw extruder (Bradender®) at 160°C, with a retention
time of 3 minutes. The number average molecular weight
for the dried control sample dropped from an initial
20 value of 44,000 to a final value of 33,000 for the 306
ppm water sample and to 28,000 for the 700 ppm water
sample. The test sample number average molecular weight
dropped from an initial value of 40,000 to a final value
of 33,000.

25   This sample shows how the water scavenger
protected the polymer from moisture pick-up, imparting
the same stability as a thorough drying of the control
sample. Combining a water scavenger with appropriate
drying is expected to give even greater stability.

30

EXAMPLE 14:

Optimization of Catalyst Concentration

A mixture of 80% L-lactide and 20% D,L-lactide
was polymerized using three different levels of tin(II)
35 bis(2-ethyl hexanoate) catalyst. Batches were prepared
at monomer/catalyst molar ratios of 1000:1, 3000:1, and
20,000:1. Polymerization times were adjusted to reach

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high conversion without being excessively long and
thereby causing degradation in the melt. The reaction
times were 1,2 and 20 hours, respectively. The
polymerization temperature was 180°C. The polymers were
5 ground to a coarse powder and devolatilized at 125°C and
10 mm Hg overnight. The samples were then reground and
1-gram portions of each were placed into silanized
vials, 16 ml capacity. The vials were sealed and placed
into an oil bath at 180°C. Vials were then removed at
10 various times and the samples were analyzed by GPC after
dissolution in chloroform. The molecular weights and
lactide contents are shown below in Table 16.

TABLE 16

Sample Lactide	Time	Number Average	Weight Average	
%	(min)	Molecular Weight	Molecular Weight	Weight
1000:1	0	39,000	81,300	0.8
	5	28,100	57,300	2.4
	15	25,800	49,700	2.8
	30	23,100	43,800	3.7
	60	22,800	43,200	3.6
3000:1	0	53,100	113,600	0.6
	5	39,000	76,400	0.4
	15	30,300	65,400	1.9
	30	29,000	60,400	2.7
	60	28,200	55,200	2.8
20000:1	0	89,200	184,000	0.0
	5	81,200	165,100	0.0
	15	54,300	134,600	0.1
	30	51,100	119,600	0.0
	60	49,500	111,000	0.0

These results show the benefit of optimizing
40 the catalyst level used in the polymerization process.
Note that both lactide reformation and molecular weight
retention benefits are realized from the reduced
catalyst levels (higher monomer/catalyst ratio).

It is believed catalyst levels should be
limited to 1000:1 for the high end of catalyst usage,
with 3000:1 being more preferable and showing somewhat
improved stability. Lower levels still, such as
5   20000:1, show greatly improved stability. Beyond this
level it is believed the polymerization rates become too
slow to be practical.

                        EXAMPLE 15:
10 Removal of Tin Catalyst from Polylactide by Precipitation
            45 grams of L-lactide and 13 grams of D,L-
    lactide were charged with 78 milligrams of crystalline
    lactic acid to a 200 ml round bottom flask. This was
    heated to 180°C with magnetic stirring in an oil bath
15 and blanketed with dry nitrogen. Catalyst in the form
    of tin(II) bis(2-ethyl hexanoate) was added as 0.20 ml
    of a 0.47 g/ml solution in THF after the molten lactide
    was at temperature. The mixture was allowed to stir for
    one minute and then pipetted into 3 silanized glass
20 vials, which were then sealed and placed into a 180°C
    oil bath for 75 minutes. The vials were allowed to cool
    and the polymer recovered by breaking the glass. The
    polymer was ground to a coarse powder and dissolved in
    chloroform to make a 10% solution. The polymer
25 contained 3.8% residual monomer and had a number average
    molecular weight of 70,000 as determined by GPC
    measurement (the method of Example 1).
            500 ml of methanol were placed in a 1-liter
    glass blender flask. The blender was turned on to
30 medium speed and 50 ml of the polymer in chloroform
    solution was poured in over a period of three minutes.
    After one additional minute of blending the mixture was
    filtered, then rinsed with 100 ml of methanol, and dried
    overnight under vacuum. The polymer consisted of a
35 fibrous mat. It contained 0.3% residual monomer and had
    a number average molecular weight of 66,900.

The measured tin level in the precipitated
polymer was 337 ppm. by weight, compared to a calculated
value of 466 ppm for the as-produced polymer. This
result indicates the feasibility of reducing residual
5 catalyst levels in lactide polymers by solvent
precipitation with the benefit of improved stability as
detailed in Example 14.

                        EXAMPLE 16:
10   <u>Melt-Processability Versus Molecular</u>
                 <u>Weight and Viscosity</u>
           The Melt Flow Index (MI) is specified by ASTM
method D-1238 and is frequently used as a practical
measure of viscosity for processing applications.
15 Higher melt flow index corresponds to lower viscosity.
Desired values of the melt flow index range from 0.1-2
for a typical extrusion operation, 10-20 for film
extrusion or for paper coating, and 1-10 for injection
molding.
20   Based on capillary viscometer measurements the
applicants have estimated melt flow index as a function
of temperature and molecular weight, with results shown
below in Table 17.

25   TABLE 17

Number Average Molecular Weight	Weight Average Molecular Weight	Melt Flow Index (Calc)		
		@ 150°C	@175°C	@200°C
50,000	100,000	75	1600	36000
75,000	150,000	18	400	9000
100,000	200,000	6	140	3000
150,000	300,000	1.5	34	800
200,000	400,000	0.6	13	300
250,000	500,000	0.3	6	120
300,000	600,000	0.1	3	70

           High temperature processing of polylactide is
undesirable because both lactide reformation and
40 molecular weight reductions become more severe as
temperature increases. The effect of temperature on

degradation is shown, for example, by Jamshidi et al., Polymer, vol. 29, pp. 2229-2234 (1988), incorporated herein by reference, and detailed in prior experimental examples. Acceptable temperature ranges vary with the

5 stability of the polymer and the processing temperature.

       The table above indicates that for unstabilized polymers, which might be processed at 150°C, an upper limit of 100,000 for the number average molecular weight would be appropriate to achieve a melt flow index near

10 10 (as might be used for injection molding). For slightly stabilized polymers, which could be processed at 175°C without degradation or lactide reformation, the number average molecular weight could be as high as 250,000 with a weight average molecular weight of

15 500,000. For the most stabilized polymers, which could be processed at 200°C or higher, the molecular weight will be limited only by purity of the lactide. Applications which can operate at lower melt flow indices will have greater tolerance for higher molecular

20 weight.

       Note that these processing temperatures are approximations for post-processing, and that the devolatilization operation will frequently be carried out at higher temperatures in order to effectively

25 remove the lactide.

       It will be understood, however, that even though these numerous characteristics and advantages of the invention have been set forth in the foregoing description, together with details of the structure and

30 function of the invention, the disclosure is illustrative only, and changes may be made in detail, especially in matters of shape, size and arrangement of the parts or in the sequence or the timing of the steps, within the broad principle of the present invention to

35 the full extent indicated by the broad general meaning of the terms in which the appended claims are expressed.

WHAT IS CLAIMED IS:

        1.   A melt-stable lactide polymer composition,
    comprising:
            (a) a mixture of polylactide material
        having a number average molecular weight of at
        least 10,000; said mixture containing a
        residual monomer concentration of lactide of
        less than about 2% by weight;
            (b) stabilizer to depolymerization of the
        polylactide in an amount effective to
    inhibit generation of lactide sufficiently
    such that a devolatized sample of the mixture
    will comprise less than 2% by weight lactide,
    after exposure to a temperature of 180°C for 15
    minutes.

        2.   A melt-stable lactide polymer composition
    according to claim 1 wherein:
            (a) said mixture of polylactide material
        comprises a reation product of a lactide
        mixture comprising:
                (i)   5-50% by weight meso-lactide;
                and,
                (ii) an effective amount of L-
                lactide.

        3.   A composition according to claim 1
    wherein:
            (a) said stabilizer is selected from the
        group consisting essentially of: antioxidants;
        water scavengers; and, mixtures thereof.

    4.   A composition according to claim 1 wherein:
            (a) said polylactide material comprises
        polylactide chains having a number average
        molecular weight within the range of about

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15,000 to about 150,000.

5.   A melt-stable lactide polymer composition
according to claim 1 wherein:
          (a)   said mixture of polylactide material
      comprises polylactide polymer chains, said
      plurality having a number average molecular
      weight of from about 10,000 to about 300,000;
          (b)   said mixture includes no more than
      1000 parts-per-million water; and
          (c)   said stabilizing agent is present in
      an amount sufficient to reduce depolymerization
      of said plurality of polylactide polymer chains
      during melt-processing, such that the
      generation of lactide is less than about 2% by
      weight of the composition from a devolatilized
      sample in the first hour at a temperature of
      180°C and atmospheric pressure.

6.   The melt-stable lactide polymer
composition of claim 5, wherein the plurality   of
polylactide polymer chains are the reaction product
of polymerizing a lactide mixture comprising about
5% by weight to about 50% by weight meso-lactide and
about 95% by weight or less L-lactide.

7.   The melt-stable lactide polymer
composition of claim 5, wherein the plurality of
polylactide polymer chains have a number average
molecular weight from about 15,000 to about 150,000.

8.   The melt-stable lactide polymer
composition of claim 5, wherein the lactide
concentration is less than about 0.5% by weight.

9.   The melt-stable lactide polymer
composition of claim 5, wherein the stabilizing

agent is an antioxidant.

10. The melt-stable lactide polymer
composition of claim 9, wherein the antioxidant is a
phosphite-containing compound.

11. The melt-stable lactide polymer
composition of claim 9, wherein the antioxidant is a
hindered phenolic or phenolic compound.

12. The melt-stable lactide polymer
composition of claim 9, wherein the antioxidant is
selected from the group consisting of: trialkyl
phosphites, mixed alkyl/aryl phosphites, alkylated
aryl phosphites, sterically hindered aryl
phosphites, aliphatic spirocyclic phosphites,
sterically hindered phenyl spirocyclics, sterically
hindered bisphosphonites, hydroxyphenyl propionates,
hydroxy benzyls, alkylidene bisphenols, alkyl
phenols, aromatic amines, thioethers, hindered
amines, hydroquinones and mixtures thereof.

13. The melt-stable lactide polymer
composition of claim 5, wherein the stabilizer
comprises a water scavenger selected from the group
consisting of: carbodiimides, anhydrides, acyl
chlorides, isocyanates, alkoxy silanes and mixtures
thereof.

14. The melt-stable lactide polymer
composition of claim 5, wherein the stabilizer
includes a disiccant selected from the group
consisting of: clay, alumina, silica gel, zeolites,
calcium chloride, calcium carbonate, sodium sulfate,
bicarbonates and mixtures thereof.

15.   A composition according to claim 5

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including residual catalyst in a molar ratio of
monomer to catalyst as greater than about 3000:1.

    16. A process for the manufacture of a melt-
stable lactide polymer composition, comprising the
steps of:

        (a) providing a lactide mixture, wherein
    said mixture contains: about 5% by weight to
    about 50% by weight meso-lactide; and, L-
    lactide;

        (b) polymerizing said lactide mixture to
    form polylactide;

        (c) adding a stabilizing agent in an
    amount sufficient to reduce depolymerization of
    polylactide during melt-processing such that
    the generation of lactide is less than about 2%
    by weight of the composition from a
    devolatilized sample in the 15 minutes at a
    temperature of 180°C and atmospheric pressure;
    and

        (d) devolatilizing the polylactide to
    reduce any presence of unreacted monomer and
    residual water.

    17. The process of claim 16, further
comprising the step of adding a catalyst
deactivating agent subsequent to polymerizing said
lactide mixture.

    18. The process of claim 16, wherein the
polymerizing is conducted at a temperature of at
least 160°C.

    19. The process of claim 16, including a step
of adding a molecular weight control agent in an
amount sufficient that the polylactide formed has a
number average molecular weight of between about

10,000 and about 200,000.

    20. The process of claim 16, wherein the step
of devolatilizing includes reducing any
concentration of unreacted lactide to less than
about 2% by weight of the polylactide and any
concentration of water to less than about 1000
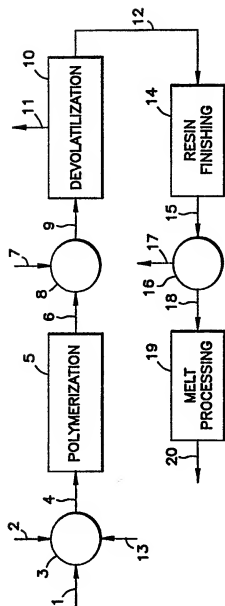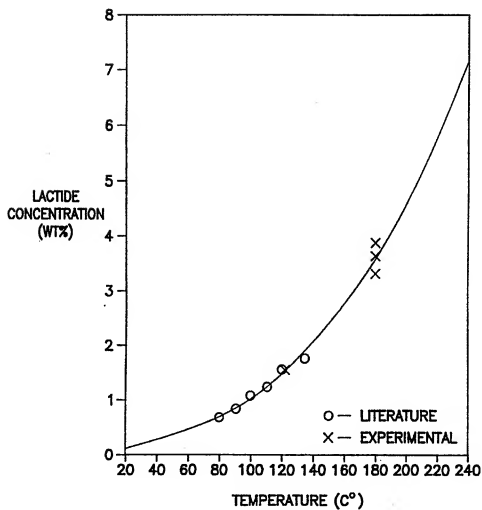parts-per-million of the polylactide.

FIG. 1

FIG. 2

INTERNATIONAL SEARCH REPORT

A. CLASSIFICATION OF SUBJECT MATTER
IPC 5   C08K11/00   C08L67/04   C08G63/08

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 5   C08K   C08L   C08G

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category°	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
E	US,A,5 252 646 (IOVINE ET AL.) 12 October 1993 see table 2 see claims 1-4 ---	1-4
X	DATABASE WPI Derwent Publications Ltd., London, GB; AN 68-03745Q & JP,B,43 008 614 (DAICEL LTD) 3 April 1968 see abstract ---	1-4
X	DATABASE WPI Derwent Publications Ltd., London, GB; AN 68-00574Q & JP,B,43 003 017 (DAICEL LTD) 3 February 1968 see abstract ---	1-4

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| X | Further documents are listed in the continuation of box C. | | X | Patent family members are listed in annex. |

° Special categories of cited documents :

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Date of the actual completion of the international search	Date of mailing of the international search report
20 January 1994	10. 02. 94

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European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax (+31-70) 340-3016	Siemens, T

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	DATABASE WPI Derwent Publications Ltd., London, GB; AN 68-00558Q & JP,B,43 002 949 (DAICEL LTD) 2 February 1968 see abstract	1-5,13
X	GB,A,1 161 932 (SHELL INTERNATIONALE RESEARCH MAATSCHAPPIJ) 20 August 1969 see page 1, line 49 - line 55 see claims 1-7,12,14	1-5,9

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